Macrocyclic Polyphosphane Ligands. Cobalt(II) and Nickel(II) Complexes of the γ and ε Diastereoisomers of 4,7,13,16-Tetraphenyl-4,7,13,16-tetraphospha-1,10-dithiacyclo-octadecane (L^1) and the Crystal Structure of $[Co(\varepsilon\text{-}L^1)][BPh_4]_2\cdot EtOH$ †

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The chiral configuration of the title diastereoisomer, ε-L^1, has been ascertained by the *X*-ray crystal-structure determination of its cobalt(II) complex $[Co(\varepsilon\text{-}L^1)][BPh_4]_2\cdot EtOH$. The complex crystallises in the monoclinic space group $P2_1/c$, with a = 14.590(3), b = 13.004(3), c = 40.972(9) Å, β = 91.80(4)°, and Z = 4. Least-squares refinement gave R = 0.114 for 1 241 observed reflections. The cobalt atom is six-co-ordinated by two sulphur and four phosphorus atoms of the macrocycle forming a distorted *cis*-octahedral geometry. The nickel complexes are attributed a similar stereochemistry on the basis of their electronic spectra. The stereochemistry of the cobalt and nickel complexes of γ-L^1 has been investigated by electronic spectroscopy. The γ-L^1 isomer behaves as a quadridentate tetraphosphane ligand, the two sulphur atoms being unco-ordinated.

Our systematic investigations of the co-ordinative behaviour of the tetraphosphane macrocycles containing two additional donors (E) have often illustrated a marked interdependence between the chiral configuration of the five diastereoisomers of the same macrocycle and the co-ordination geometry of their metal complexes (Figure 1).[1–9] Thus, the different diastereoisomers of the dioxatetraphospha-macrocycle L^2 all give an essentially planar arrangement of the four phosphorus atoms around cobalt(II) and nickel(II) which, in turn, does not allow the E donors(s) to co-ordinate. Hence, octahedral,[2,3] square-pyramidal,[2] or square-planar [3,4] complexes occur.

In order to increase the donor ability of the E atoms towards low-spin complex formation, the tetraphosphadithia-macrocycle L^1 was prepared.[6] The higher 'softness' of the thioethereal donors with respect to the ethereal ones was expected to increase the competitiveness of the two sulphur donors in comparison to the phosphorus donors, possibly leading to an increased denticity of the ligand as well as to a non-planar P_4 arrangement. Actually, with the previously described α-, β-, and δ-L^1 diastereoisomers[6,7] it was found that the co-ordinative behaviour was markedly different both between themselves and also with respect to the ethereal analogues L^2. Thus, cobalt(II) and nickel(II) form complexes which are elongated *trans*-octahedral (β-L^1),[6] square-pyramidal (α-L^1),[6] and trigonal-bipyramidal (δ-L^1).[7]

The present work aims to complete the stereochemical study on the cobalt(II) and nickel(II) complexes of the whole series of the five diastereoisomers. We report here the results of the investigation on the complexes of the remaining isomers γ-L^1 and ε-L^1.

Experimental

Preparation of the Compounds.—The ligands were prepared as previously described.[6] The metal complexes were obtained with minor modifications of previously described procedures.[3,5]

Physical Measurements.—Visible and u.v. spectra were recorded on solutions with a Cary 17 and on solids with a Beckman DK-2 spectrophotometer. Magnetic susceptibility measurements were carried out with a Faraday balance. $^{31}P\text{-}\{^1H\}$ N.m.r. spectra were recorded at 20 °C on a Varian CFT 20 spectrometer operating at 31.19 MHz with proton-noise decoupling and a deuterium lock. The solvent was CD_3OD (Merck, 99.8%) unless otherwise stated. Shifts were referenced against external H_3PO_4 (85%). Electric conductivity values were measured on a WTW conductance bridge at 25 °C in methyl cyanide. Concentrations of the solutions were *ca.* 10^{-3} mol dm^{-3}.

The analytical and physical data of the compounds are summarised in Table 1.

Crystallographic Studies.—All *X*-ray measurements were performed on a Philips PW 1 100 diffractometer using Mo-K_α radiation (λ = 0.710 7 Å). Crystal data and intensity collection procedures are reported in Table 2.

Data Collection.—Several light green prisms, obtained from ethanol and *NN*-dimethylformamide, were successively mounted. All showed low diffracting power, probably due to poor crystallinity and/or large atomic thermal motion. A crystal with approximate dimensions 0.1 × 0.05 × 0.4 mm was finally chosen for data collection, but, of the 6 056 reflections measured only 1 241 had intensity greater than 2.5σ(*I*). Intensities were corrected for Lorentz and polarisation effects but not for absorption.

The structure was solved by means of Patterson and electron-density syntheses, which gave the positions of all the non-hydrogen atoms. Refinement was performed by the least-

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† *Supplementary data available* (No. SUP 56203, 8 pp.): full list of bond lengths and angles, least-squares plane data, thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

Non-S.I. unit employed: B.M. = 0.927 × 10^{-23} A m^2.

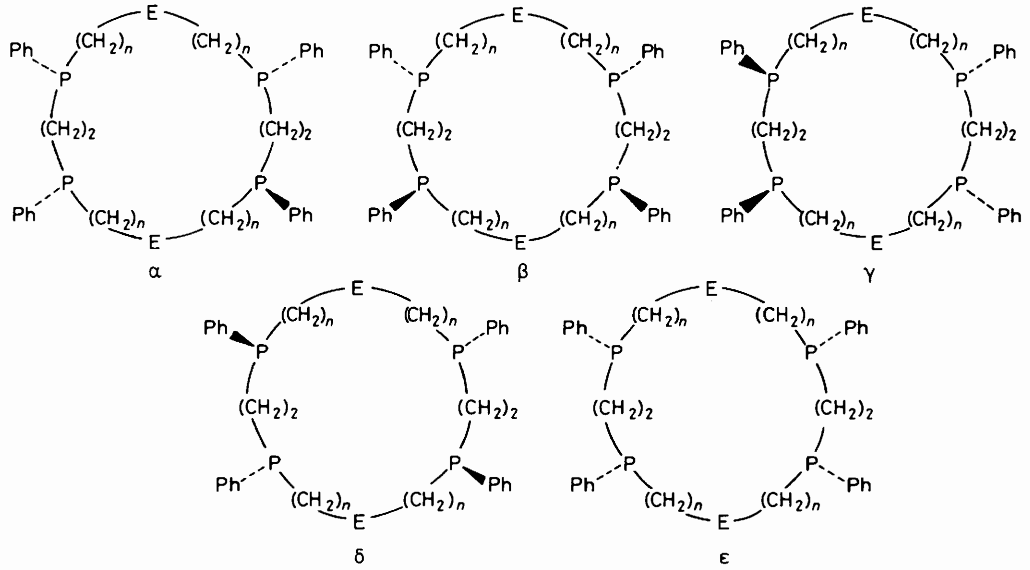

Figure 1. The five diastereoisomers of L [$n = 2$, E = S (L^1); $n = 2$, E = O (L^2); $n = 2$, E = NPr (L^3); $n = 3$, E = S (L^4)]

Table 1. Analytical and physical data for some complexes of L^1

Compound	Colour	Analysis[a] (%) C	H	Electronic spectra, ν/cm^{-1}
$[Co(\varepsilon\text{-}L^1)][BPh_4]_2$	Green	73.9 (74.05)	6.3 (6.20)	11 800, 19 000, 25 600
$[Ni(\varepsilon\text{-}L^1)][BPh_4]_2$	Red-brown	74.0 (74.10)	6.2 (6.20)	18 300, 22 700
$[Ni(\varepsilon\text{-}L^1)]Br_2{\cdot}H_2O$	Red	47.8 (48.00)	5.0 (5.15)	
$[CoCl(\gamma\text{-}L^1)][BPh_4]$	Orange	66.6 (66.80)	6.2 (6.00)	9 100, 16 600 (sh), 22 200
$[CoBr(\gamma\text{-}L^1)]Br{\cdot}H_2O$	Green	48.5 (47.95)	5.2 (5.15)	7 400, 8 500 (sh), 15 400, 22 700, 26 700
$[Ni(\gamma\text{-}L^1)][BF_4]_2{\cdot}2H_2O$	Orange	46.6 (46.30)	5.3 (5.20)	26 000 (sh)
$[NiCl(\gamma\text{-}L^1)][BPh_4]$[b]	Orange	67.0 (66.80)	6.2 (6.00)	23 000
$[NiBr(\gamma\text{-}L^1)]Br{\cdot}H_2O$	Red-brown	48.3 (47.95)	5.1 (5.15)	22 200

[a] Calculated values are given in parentheses. [b] Molar conductance for 10^{-3} mol dm^{-3} solution at 20 °C in MeCN is 93 Ω^{-1} cm^2 mol^{-1}.

Table 2. Crystal data and intensity collection procedure for $[Co(\varepsilon\text{-}L^1)][BPh_4]_2{\cdot}EtOH$

Formula	$C_{84}H_{84}B_2CoP_4S_2{\cdot}C_2H_5OH$
M	1 408.24
Crystal symmetry	Monoclinic
Space group	$P2_1/c$
a/Å	14.590(3)
b/Å	13.004(3)
c/Å	40.972(9)
β/°	91.80(4)
U/Å^3	7 769.7
Z	4
D_c/g cm^{-3}	1.21
F(000)	2 972
μ(Mo-K_α)/cm^{-1}	3.63
λ(Mo-K_α)/Å	0.7107
Monochromatisation	Graphite monochromator
Scan type	θ—2θ symmetric
Scan width/°	1.00
Scan speed/° s^{-1}	0.06
$\theta_{max.}$/°	22.5
Number of unique intensities [$I > 2.5\sigma(I)$]	1 241

squares technique, with isotropic thermal parameters for all the atoms. The function minimised was $\Sigma w(|F_o| - |F_c|)^2$ with weights $w = k/\sigma^2(F)$, where k is an adjustable parameter.

In order to reduce the number of parameters, rigid group refinement was used for all the 12 independent benzene rings. In this way a total of 248 parameters were refined, the ratio between number of reflections and number of parameters being *ca.* 5.

The final electron-density difference synthesis showed the presence of six low-intensity peaks, which were attributed to solvent molecules. Two ethanol molecules, with occupancy factors of 0.5, were then refined with fixed C–C and C–O distances. The final R and R' factors were respectively 0.114 and 0.102 $\{R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^{\,2}]^{\frac{1}{2}}\}$.

All calculations were carried out with the SHELX 76 [10] set of programs. Table 3 gives the final atomic co-ordinates with estimated standard deviations obtained from the least-squares inverse matrix. The molecular plot in Figure 2 was produced by ORTEP.[11]

Results and Discussion

Complexes of ε-L^1.—The complex $[Co(\varepsilon\text{-}L^1)][BPh_4]_2$ is low-spin, with a room-temperature $\mu_{eff.}$ value of 2.27 B.M. Its e.s.r. spectrum gives $g_\perp = 2.13$, $g_\parallel = 2.24$, and $A_\parallel = 0.005\,06$ cm^{-1}, indicative of a $d_{x^2-y^2}$ (or d_{xy}) ground state for the cobalt atom. The electronic spectrum of this complex both in the solid and in methyl cyanide solution is different from those of the low-spin cobalt(II) complexes of the other isomers α-, β-, and δ-L^1 (refs. 6 and 7) having square-pyramidal, *trans*-octahedral, and trigonal-bipyramidal geometries, respectively (Figure 3).

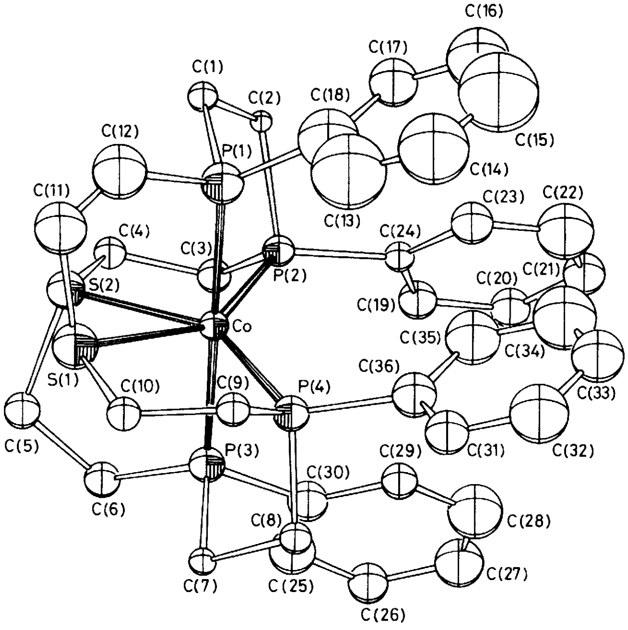

Figure 2. ORTEP drawing of the complex cation $[Co(\varepsilon\text{-}L^1)]^{2+}$ with the atom labelling scheme

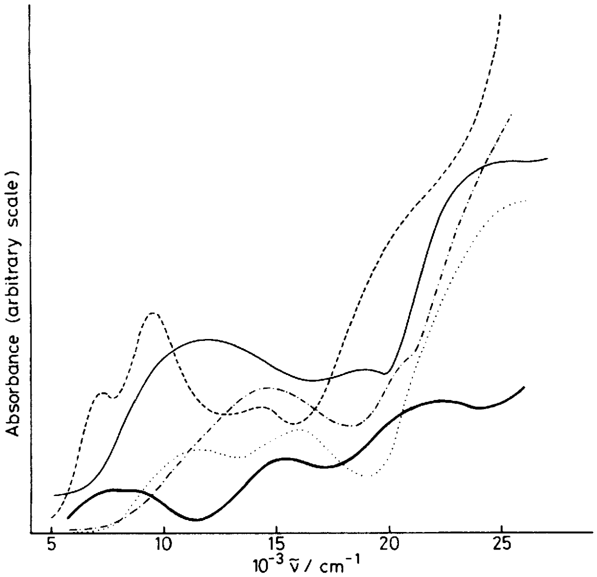

Figure 3. Solid reflectance spectra of $[Co(\alpha\text{-}L^1)][BPh_4]_2$ (– – – –), $[Co(\beta\text{-}L^1)][BPh_4]_2$ (— · — · —), $[CoCl(\gamma\text{-}L^1)][BPh_4]$ (——), $[Co(\delta\text{-}L^1)][BPh_4]_2{\cdot}2Me_2CO$ (· · · ·), and $[Co(\varepsilon\text{-}L^1)][BPh_4]_2{\cdot}EtOH$ (——)

The spectrum of $[Co(\varepsilon\text{-}L^1)][BPh_4]_2$ is also different from those of planar cobalt(II) complexes.[12] Since, in this case, the spectroscopic evidence fails positively to diagnose the co-ordination geometry, an *X*-ray structural analysis has been performed on the complex $[Co(\varepsilon\text{-}L^1)][BPh_4]_2{\cdot}EtOH$.

The structure consists of $[Co(\varepsilon\text{-}L^1)]^{2+}$ cations, $[BPh_4]^-$ anions, and lattice ethanol molecules. Figure 2 shows an ORTEP drawing of the complex cation, which contains a low-spin cobalt(II) atom in a highly distorted *cis*-octahedral stereochemistry. Table 4 reports bond lengths and angles with estimated standard deviations in the co-ordination polyhedron. Distortions in the co-ordination octahedron are found both in the angles P(2)–Co–P(4) [127.7(6)°] and S(1)–Co–S(2) [75.1(5)°], and in the distances, with the axial Co–P(1) and Co–P(3) bonds clearly shortened in comparison with the other four in-plane distances. The compressed structure accounts for the e.s.r. data which show the occurrence of an empty d_{z^2} orbital in the ground state. In particular, the Co–S bond distances appear to be rather long, their mean value of 2.59 Å being longer by 0.08 Å with respect to the value found in the *trans*-octahedral $[Co(\delta\text{-}L^4)]^{2+}$ ion.[9] The atoms P(2), P(4), S(1), and S(2) are not exactly coplanar with the cobalt atom, the deviations from the least-square plane being −0.25, +0.24, −0.32, +0.33 Å, respectively.

Although the low-spin octahedral cobalt(II) stereochemistry should be Jahn–Teller distorted, the deviations from O_h symmetry in the present case are too large to be accounted for by this effect. On the other hand it should be noted that the configuration of the ligand, which wraps around the cobalt atom, is such that all the phenyl groups lie on the same side with respect to cobalt. This obviously causes large overcrowding which might be partly responsible for the widening of the P(2)–Co–P(4) angle. Inspection of Table 4(*c*) shows, in fact, the presence of several short contacts among the carbon atoms of the phenyl groups. Most of them can be attributed to strong stacking interactions between the benzene rings attached to P(3) and P(2) and between those bound to P(1) and P(4). These rings are in fact parallel as shown by the values of the angles between the least-squares planes through them [5.4 and 7.6°, respectively, for the pair of rings bound to P(2) and P(3) and those bound to P(1) and P(4)]. These stacking interactions form an important contribution to the stabilisation of the actual conformation of the complex cation. Moreover, a repulsive contact between C(23) and C(35) can be noted.

The diamagnetic nickel complexes $[Ni(\varepsilon\text{-}L^1)]X_2$ (X = Br or BPh_4) have similar ligand-field spectra both in solution and in the solid state. The solution spectra exhibit a band at 18 700 cm^{-1} and a very broad band with a plateau between 24 700 and 27 000 cm^{-1}, which reveals the envelope of at least two transitions (Figure 4). As for the cobalt derivative the spectrum of the $[Ni(\varepsilon\text{-}L^1)]^{2+}$ species shows marked spectral differences in the number, frequencies, and intensities of the bands with the spectra of the α-, β-, and δ-L^1 complexes having square-pyramidal, elongated *trans*-octahedral, and trigonal-bipyramidal stereochemistry, respectively (Figure 3).[6,7] Moreover, the spectrum of $[Ni(\varepsilon\text{-}L^1)]^{2+}$ indicates a non-planar stereochemistry. In view of these spectroscopic differences we can tentatively attribute the $[Ni(\varepsilon\text{-}L^1)]^{2+}$ complex a stereochemistry similar to that of the cobalt analogue, *i.e.*, a distorted *cis*-octahedral geometry. The insensitivity of the ligand-field spectra to the nature of the anion indicates effective screening of the nickel ion by the macrocycle.

The $^{31}P\text{-}\{^1H\}$ n.m.r. spectra of these nickel complexes show a single resonance at 64.0 p.p.m. in methanol at room temperature (65.8 p.p.m. at −80 °C), indicating equivalence of the four phosphorus atoms on the n.m.r. time-scale over this temperature range.

Complexes of γ-L^1.—With the γ isomer the presence of at least one co-ordinating anion per cobalt atom is necessary in order to obtain isolable compounds. The reflectance spectra of these complexes are typical of square-pyramidal co-ordination. This is in line with the peculiar chiral configuration of the γ isomer which has *cis*-$P(CH_2)_2P$ and *trans*-$P(CH_2)_2E(CH_2)_2P$ moieties. Molecular models[2,3] as well as the *X*-ray structure determinations[5] of the nickel and cobalt complexes of L^3 show that such isomers cannot wrap themselves around a metal ion by co-ordinating both E and P heteroatoms. Actually, in every case examined,[3,5] it has been found that the γ isomers act as quadridentate phosphane ligands with a near-planar P_4 arrangement, the two E atoms being unco-ordinated and

Table 3. Fractional atomic co-ordinates (× 10^4) with estimated standard deviations in parentheses, for $[Co(\varepsilon\text{-}L^1)][BPh_4]_2{\cdot}EtOH$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Co	1 885(5)	2 218(5)	1 257(2)	C(B7)	9 332(26)	2 024(21)	4 483(9)
P(1)	1 936(12)	1 213(13)	814(4)	C(B8)	10 147(26)	2 318(21)	4 341(9)
P(2)	2 549(10)	799(10)	1 513(4)	C(B9)	10 558(26)	3 253(21)	4 426(9)
P(3)	1 856(10)	3 156(11)	1 707(4)	C(B10)	10 153(26)	3 894(21)	4 653(9)
P(4)	2 627(11)	3 682(12)	1 058(4)	C(B11)	9 337(26)	3 600(21)	4 795(9)
S(1)	502(11)	3 061(13)	933(4)	C(B12)	8 927(26)	2 665(21)	4 710(9)
S(2)	458(10)	1 355(11)	1 480(4)	C(B13)	8 735(20)	580(30)	5 073(8)
C(1)	1 758(31)	−106(34)	932(12)	C(B14)	8 754(20)	−436(30)	5 182(8)
C(2)	2 356(26)	−374(31)	1 253(10)	C(B15)	7 938(20)	−984(30)	5 208(8)
C(3)	1 945(33)	462(35)	1 873(12)	C(B16)	7 102(20)	−516(30)	5 126(8)
C(4)	912(31)	358(35)	1 770(11)	C(B17)	7 083(20)	500(30)	5 016(8)
C(5)	51(31)	2 355(39)	1 763(11)	C(B18)	7 899(20)	1 048(30)	4 990(8)
C(6)	855(30)	2 872(36)	1 963(11)	C(B19)	7 918(20)	2 672(26)	5 535(14)
C(7)	1 809(29)	4 562(32)	1 610(11)	C(B20)	7 831(20)	3 363(26)	5 792(14)
C(8)	2 687(32)	4 765(34)	1 336(12)	C(B21)	7 478(20)	4 345(26)	5 733(14)
C(9)	2 026(35)	4 279(36)	704(12)	C(B22)	7 212(20)	4 635(26)	5 416(14)
C(10)	953(34)	4 271(36)	737(12)	C(B23)	7 299(20)	3 944(26)	5 159(14)
C(11)	325(42)	2 209(54)	579(16)	C(B24)	7 652(20)	2 963(26)	5 218(14)
C(12)	910(49)	1 538(56)	548(18)	B(2)	7 914(35)	2 299(43)	2 667(13)
C(13)	3 594(56)	288(40)	618(10)	C(B25)	6 544(23)	1 086(24)	2 807(7)
C(14)	4 408(56)	303(40)	449(10)	C(B26)	5 762(23)	819(24)	2 975(7)
C(15)	4 586(56)	1 110(40)	236(10)	C(B27)	5 323(23)	1 551(24)	3 163(7)
C(16)	3 950(56)	1 903(40)	192(10)	C(B28)	5 666(23)	2 551(24)	3 184(7)
C(17)	3 136(56)	1 889(40)	362(10)	C(B29)	6 449(23)	2 819(24)	3 016(7)
C(18)	2 958(56)	1 081(40)	575(10)	C(B30)	6 888(23)	2 086(24)	2 828(7)
C(19)	3 949(27)	529(23)	2 007(10)	C(B31)	7 783(18)	1 721(20)	2 042(10)
C(20)	4 861(27)	441(23)	2 116(10)	C(B32)	7 942(18)	998(20)	1 799(10)
C(21)	5 560(27)	417(23)	1 891(10)	C(B33)	8 436(18)	106(20)	1 874(10)
C(22)	5 346(27)	481(23)	1 558(10)	C(B34)	8 771(18)	−64(20)	2 192(10)
C(23)	4 434(27)	570(23)	1 449(10)	C(B35)	8 612(18)	659(20)	2 435(10)
C(24)	3 736(27)	593(23)	1 673(10)	C(B36)	8 118(18)	1 552(20)	2 360(10)
C(25)	2 747(22)	3 122(23)	2 335(12)	C(B37)	8 641(20)	4 137(31)	2 451(8)
C(26)	3 505(22)	3 126(23)	2 552(12)	C(B38)	8 618(20)	5 116(31)	2 313(8)
C(27)	4 389(22)	3 091(23)	2 432(12)	C(B39)	7 787(20)	5 531(31)	2 198(8)
C(28)	4 515(22)	3 050(23)	2 096(12)	C(B40)	6 979(20)	4 967(31)	2 222(8)
C(29)	3 757(22)	3 046(23)	1 880(12)	C(B41)	7 002(20)	3 987(31)	2 361(8)
C(30)	2 873(22)	3 081(23)	2 000(12)	C(B42)	7 833(20)	3 572(31)	2 475(8)
C(31)	4 131(34)	4 497(30)	749(11)	C(B43)	8 570(14)	2 383(20)	3 268(9)
C(32)	5 010(34)	4 479(30)	625(11)	C(B44)	9 248(14)	2 452(20)	3 515(9)
C(33)	5 585(34)	3 640(30)	688(11)	C(B45)	10 171(14)	2 472(20)	3 436(9)
C(34)	5 281(34)	2 820(30)	875(11)	C(B46)	10 416(14)	2 422(20)	3 110(9)
C(35)	4 402(34)	2 838(30)	1 000(11)	C(B47)	9 738(14)	2 351(20)	2 863(9)
C(36)	3 827(34)	3 677(30)	937(11)	C(B48)	8 815(14)	2 331(20)	2 942(9)
B(1)	7 906(40)	2 322(50)	4 881(15)	C(1S)*	1 711(52)	9 939(51)	3 755(18)
C(B1)	7 183(17)	2 345(24)	4 249(10)	C(2S)	2 414(52)	9 111(51)	3 665(18)
C(B2)	6 469(17)	2 389(24)	4 016(10)	O(S)	848(52)	9 695(51)	3 617(18)
C(B3)	5 564(17)	2 476(24)	4 113(10)	C(1S′)	3 058(57)	3 140(53)	3 771(24)
C(B4)	5 375(17)	2 519(24)	4 444(10)	C(2S′)	2 715(57)	2 515(53)	3 473(24)
C(B5)	6 090(17)	2 475(24)	4 678(10)	O(S′)	2 745(57)	2 693(53)	4 058(24)
C(B6)	6 994(17)	2 388(24)	4 581(10)				

* S = Solvent.

pointing away from the metal. Such an arrangement leaves the metal ion rather unscreened, thus possibly allowing co-ordination of halide ions or solvent molecules. Due to the well known reluctance of cobalt(II) to form low-spin square-planar complexes,[13] one halide ion does co-ordinate giving square-pyramidal compounds.

With nickel a square-planar NiP_4 chromophore is present in the complex $[Ni(\gamma\text{-}L^1)][BF_4]_2$, as shown by its reflectance spectrum ($\nu_{max.} = 26\,000$ cm^{-1}). On the contrary, the nickel complexes with co-ordinating anions (Cl^- or Br^-) show considerable red-shifts of this peak. In particular, the spectrum of $[NiCl(\gamma\text{-}L^1)][BPh_4]$ in methyl cyanide solution (essentially similar to that in the solid state) exhibits a broad asymmetric band with its maximum at 23 800 cm^{-1} ($\varepsilon = 1\,120$ dm^3 mol^{-1} cm^{-1}) (Figure 4). Gaussian analysis of this spectrum unambiguously reveals the occurrence of a peak at *ca.* 19 500 cm^{-1} ($\varepsilon \simeq 280$ dm^3 mol^{-1} cm^{-1}) beneath the main band. Such a spectrum is thus indicative of square-pyramidal co-ordination of the nickel ion, which is probably achieved by axial co-ordination of a chloride ion, since this complex behaves as a 1 : 1 electrolyte in methyl cyanide solution.

The room temperature $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum of $[NiCl(\gamma\text{-}L^1)][BPh_4]$ shows 24 lines in the range 36—65 p.p.m., the line pattern being that of an A_2B_2 type. This is in agreement with the C_s symmetry, at most, of the square-pyramidal cation due to the chiral requisites of the phosphorus atoms which, in pairs, have the phenyl groups pointing upwards and downwards from the chloride ion, respectively. It also shows a low exchange rate of the co-ordinated chloride anion on the n.m.r. time-scale.

Table 4. Bond lengths (Å) and angles (°) with estimated standard deviations in parentheses, for $[Co(\varepsilon\text{-}L^1)][BPh_4]_2\cdot EtOH$

(*a*) Bond lengths

Co–P(1)	2.24(2)	Co–P(4)	2.35(2)
Co–P(2)	2.32(1)	Co–S(1)	2.62(2)
Co–P(3)	2.21(1)	Co–S(2)	2.56(2)

(*b*) Bond angles

P(2)–Co–P(1)	83.0(6)	S(1)–Co–P(3)	99.0(6)
P(3)–Co–P(1)	177.6(7)	S(1)–Co–P(4)	80.9(6)
P(3)–Co–P(2)	94.6(6)	S(2)–Co–P(1)	94.7(6)
P(4)–Co–P(1)	99.5(6)	S(2)–Co–P(2)	79.8(5)
P(4)–Co–P(2)	127.7(6)	S(2)–Co–P(3)	84.6(6)
P(4)–Co–P(3)	82.1(6)	S(2)–Co–S(1)	75.1(5)
S(1)–Co–P(1)	83.0(6)		

(*c*) Intramolecular non-bonding distances

S(1) ••• S(2)	3.16	C(35) ••• C(23)	3.48
C(28) ••• C(19)	3.40	C(29) ••• C(24)	3.30
C(29) ••• C(20)	3.32	C(17) ••• C(35)	3.38
C(28) ••• C(20)	3.43	C(17) ••• C(36)	3.44

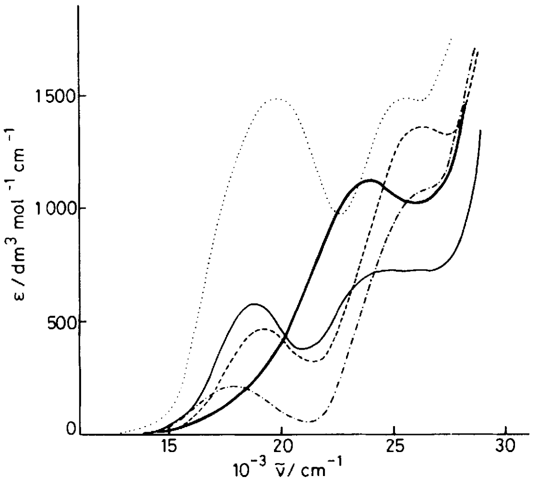

Figure 4. Absorption spectra of $[Ni(\alpha\text{-}L^1)][BPh_4]_2$ (– – – –), $[Ni(\beta\text{-}L^1)][BF_4]_2$ (— · — · —), $[NiCl(\gamma\text{-}L^1)][BPh_4]$ (**——**), $[Ni(\delta\text{-}L^1)][BPh_4]_2$ (· · · ·), and $[Ni(\varepsilon\text{-}L^1)][BPh_4]_2$ (——) in methyl cyanide

Conclusions

The series of the five diastereoisomers of L^1, described in this and previous[6,7] papers, gives an interesting example of the co-ordinative constraints imposed by the mutual chiralities of the donor atoms with these annular ligands. Such internally constrained structures can prevent complete wrapping of the metal ion so that some of the six potential donors cannot co-ordinate, as in the case of the α[6] and γ isomers.

In addition to these geometrical effects, the nature of the E donors also plays a role, due to the strong ligating ability of the P_4 group which donates four electron pairs to the metal. For cobalt(II) and nickel(II) complexes, simple electron-count considerations rule out the formation of two additional strong covalent bonds with the E donors. In fact, two long M—E interactions are present in some instances with β,[2,5,6] δ,[3] and ε diastereoisomers, which geometrically allow a six-co-ordinate structure. With the ε diastereoisomers, the fairly high donor ability of the thioethereal sulphur atoms allows two long M—S interactions in the cobalt and nickel complexes of ε-L^1, whereas no definite interaction occurs with the nickel complex of the ethereal analogue L^3.[4] On the other hand, with the δ isomers, for which meridional arrangements of the P•••E•••P moieties are requested in an octahedral metal complex,[3] long M—E distances can occur only with the smaller oxygen atom in δ-L^2,[3] or with the large 22-membered macrocycle δ-L^4.[9] On the contrary, with the 18-membered dithiamacrocycle δ-L^1 a five-co-ordinate structure results,[7] only one M—S strong bond being formed.

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